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MICROCOPY RESOLUTION TEST CHART

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MIDDLE INFRARED SPECTRAL STUDIES OF GEOLOGIC MATERIALS IN THEIR

NATURAL STATE USING PHOTOTHERMAL BEAM DEFLECTION SPECTROSCOPY*

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ABSTRACT

The use of a novel laboratory spectral technique is described for the recording of middle infrared (MIR) absorption spectra of natural surfaces with no sample preparation. Such a technique allows evaluation of spectral influences of surficial films such as weathering products, lichen cover or desert varnish on the spectra of the substrate geologic materials. In remote sensing applications the technique should provide spectral information more nearly representative of field conditions and may improve interpretation of thermal imagery. The technique, called photothermal beam deflection spectroscopy (PBDS) was originally developed for studies of surface chemistry in situations where it is impractical or impossible to separate surface layers from their substrate. In the present studies the spectral characteristics of natural rock and mineral surfaces have been examined. Sensitivity, resolution and signal-to-noise ratios are quite good. Silicate and carbonate components of sedimentary rocks are well resolved and the technique can distinguish between the aragonite and calcite modifications of calcium carbonate. Effects of such agents as lichen cover and desert varnish on the spectra of underlying rock are illustrated.

1. INTRODUCTION

Spectral data in the middle infrared (MIR) (5-20 microns) wave-length region have been shown to be useful in such remote sensing applications as rock-type[1] and thermal mapping[2]. For terrestrial studies the "atmospheric window" between 8 and 14 microns holds the most promise because it is the region of maximum thermal emission at terrestrial surface temperatures and is also the region where many rock and mineral materials exhibit their diagnostic spectral features.

Previously published laboratory MIR rock and mineral spectra suffer from certain drawbacks if the data are used in the interpretation of remotely sensed thermal imagery. Transmission studies often require a sample to be crushed and measured in a matrix material such as KBr, a process which destroys all surficial information about the sample. This is not a trivial consideration in view of the fact that surfaces are what are observed by remote sensors. If reflection techniques are used, flat polished surfaces must be prepared on samples or hemispherical collection techniques must be used to avoid loss of energy by scattering. During polishing significant natural surficial characteristics may be removed. Emission studies, being very sensitive to sample condition such as particle size and surface temperature, present measurement and interpretation problems.
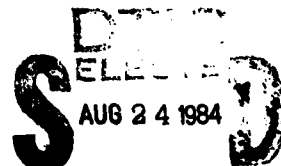
Among Lyon's[3] conclusions from his work were that absorption spectra have the highest spectral contrast and are the most definitive while emission spectra are the most difficult to interpret.

2. PROCEDURE

A variety of geologic materials including pure minerals plus several sedimentary and igneous rocks exhibiting fresh, weathered, varnished and lichen covered surfaces were examined in the 5 to 20 micron spectral region by the PBDS technique. Samples were collected in various locations by several people (Table I.) Spectral measurements were made directly on sample surfaces with no preparation or alteration.

Table I. Background Information on Rock and Mineral Samples

Sample	Origin	Collector
Coral	Shelf Sample	-
Calcite	Reagent Grade $CaCO_3$	-
Gypsum Sand	White Sands, NM	M. Satterwhite
Gypsum	Reagent Grade $CaSO_4-2H_2O$	-
Limestone	Utah	M. Kingston
Basalt	New Mexico	J. Ehlen
Kimberlite	So. Africa	M. Kingston
Altered igneous	Cuprite Mining Dist., NEV Goldfield Mining Dist, NEV	M. Kingston
Alunite	Nevada	M. Kingston
Lichen covered Siltstone	Montana	J. Eastes
Varnished sample	California	C. Breed
Weathered volcanic	Montana	J. Eastes

3. INSTRUMENTATION AND TECHNIQUE

The PBDS spectrometer[4] and technique[5] have been described in detail elsewhere, and only a general description will be repeated here.

The photothermal effect arises when incident radiation is selectively absorbed by a material and is converted to thermal energy so that the local temperature rises. With strongly absorbing materials such as rock and minerals the temperature rise occurs near or at the surface resulting in heating of the immediate surroundings. The instrument used is a modified infrared FT (Fouier transform) spectrometer fitted with a so called "mirage" detector. The latter is the basis of a novel and sensitive spectroscopic method invented by Boccara et al.[6] The mirage detector is conceptually simple and basically consists of passing a laser light beam over a sample surface which has been warmed by the incident radiation. The thermal gradient and consequent refractive index gradient in the medium over the surface causes the beam to be deflected, Fig. 1. If the incident radiation is modulated as with a chopper, sample heating and beam deflection are also modulated, and the up and down motion of the beam can be observed with position detectors. That signal is then a measure of the photothermal effect occurring at the surface. In order to permit using an optical lever to increase sensitivity without subjecting the system to extreme mechanical vibrations, the compensated system shown schematically in Fig. 1 was developed. It is based on the premise that two beams traversing nearly the

same path will be subjected to the same mechanical disturbances, so that *these can be cancelled.* The beam from a 2 mW HeNe laser is divided by a beam-splitter-cube and, after passing over almost the same optical path, each beam falls on a position-sensing detector. The detector electronics are set up so that the beam movements cancel in the absence of infrared radiation. The photothermal effect is then induced on the sample by the chopped infrared radiation from the interferometer and the photothermally induced beam deflection is picked up by the detectors.

The sample holder is illustrated in Fig. 2 and is set up so that the bottom of the probe laser beam passes slightly above the region where the infrared beam coming from the collecting mirror pass through a focus. Then in order to examine a sample, all that is necessary is to bring the sample to the infrared focus and make mechanical adjustments so that the probe beam grazes the sample surface, until the photothermal signal is maximized. The sample must have a flat area 2-3 mm in diameter accessible to the probe beam. Particulate samples (e.g. soils, sand) can be heaped on a leveling platform (Fig. 2), but it is more convenient to pack particulates into a cup-shaped receptacle fastened to the platform. The device can then be *repositioned precisely so that* it is only necessary to pack particulates into the cup and scrape off the excess so that a flat surface results. Solid samples such as rocks are simply placed on the platform and the leveling screws adjusted until the surface of the sample is in the proper position.

The output of the detectors results in a photothermal interferogram which is then processed as in a conventional FT spectrometer and results in a single-beam spectrum, S. A sample spectrum S is corrected for variations of intensity of the source radiation with wavelength and for instrument function by ratioing S against the single beam S_0 of a carbon or platinum black reference which is assumed to be a flat black absorber. The resulting compensated spectrum then shows the proper intensity ratios for absorption bands which appear as positive on the ordinate, S/S_0. Spectra shown were recorded at 8 cm^{-1} resolution, using 400-500 scans. Samples up to approximately 10x10x10 cm. can be accomodated.

4. SPECTRAL RESULTS

Mineral Spectra

Carbonates are abundant in the surface cover of the earth. $CaCO_3$ is the most abundant, occurring as limestone, chalk, cementing material in sedimentary rocks and in the shell of certain marine organisms. Fig. 3 shows spectra of two forms of this material.

Table II. Transmission Spectra Bands of Calcite and Gypsum.

	Wavelength (Microns)		Assignment			Wavelength (Microns)	Assignment
Calcite	14.12		$\nu_4(CO_3^=)$	Gypsum		16.2	$\nu_4(SO_4^=)$
	11.47		$\nu_2(CO_3^=)$			8.91	$\nu_3(SO_4^=)$
	7.0		$\nu_3(CO_3^=)$			6.17	$\nu_2(H_2O)$
	5.57	2 X	$\nu_2(CO_3^=)$			5.95	$\nu_2(H_2O)$

In this figure the band near 14 microns in the lower trace corresponds to ν_4 (Table II), that near 11.4 microns is ν_2 ,that near 7 microns is ν_3

and the small sharp band near 5.6 microns is $2\nu_2$, thus clearly identifying the material as calcite. The less symetric aragonite form of $CaCO_3$ also exhibits a band near 9.1 microns, ν_1, and the occurrence of this band in the upper spectrum of Fig. 3 indicates that the sample, a white coral, contained a significant amount of aragonite.

Hydrous calcium sulfate or gysum is common in much of the soil of the western United States. Fig. 4 shows the spectrum of reagent grade hydrous calcium sulfate together with the spectrum of naturally occurring gypsum sand from New Mexico. Bands at 5.9 and 6.2 microns originate from water of hydration; a band near 9.9 microns and a double peaked band between 14 and 15 microns corresponds to $SO_4^=$ ν_3 and ν_4 respectively.

Rock Spectra

Often the spectral features of the major minerals comprising a rock are obvious from its spectrum. This is particularly true for sedimentary rock containing carbonates and/or quartz since some of their spectral features are very pronounced and in general well separated. The spectrum of a limestone from Utah comprising together with carbonate a small amount of quartz plus a significant component of ferric oxide coated clay minerals is illustrated in the upper curve of Fig. 5. The spectrum displays carbonate features near 5.6, 6.9, 11.5, and 14 microns. The presence of silicate minerals is indicated by the appearance of the major silicon-oxygen stretching frequency near 9 microns. Quartz is always indicated by the presence of the doublet near 12.5 microns. Ferric oxide is spectrally rather featureless in the 8-14 micron region but shows strong absorption bands between 15 and 20 microns and its presence is suggested by the absorption near 20 microns.

The lower trace of Fig. 5 is a spectrum of a basalt. The most prominent feature is the silicate band centered between 9 and 10 microns; a band near 6 microns is due to water.

The upper spectrum in Fig. 6 is that of a kimberlite sample from South Africa consisting of olivine, pyronene, serpentine plus lesser amounts of carbonate, garnet and ilmenite. Total SiO_2 content is about 40%. Characteristic features for carbonate appear at 6.9 microns and several poorly resolved features centered near 10 microns are indicative of silicates. Ilmenite displays a strong band at 18.2 microns and strong absorption here is suggestive of the presence of the latter. The band around 6.1 microns is due to water.
The lower spectrum in Fig. 6 is that of a sample containing alunite, a mineral of widespread occurence in near-surface rocks of volcanic regions which have been altered by solutions of sulfuric acid. Alunite is a basic sulfate of aluminum and potassium [$KAl_3(SO_4)_2(OH)_6$]. Sulfate spectral features appear at 8.9, 14.5 and 15.9 microns. A water of hydration band is evident near 6.1 microns. The weak feature near 7 microns is attributed to the presence of NH_4^+. The latter ion may be found substituted for K+ in certain feldspars, e.g. buddingtonite, which occurs in the locale where the sample was collected. The presence of $CO_3^=$ was ruled out due to the absence of absorption near 11.5 and 14.1 microns.

Figure 7 shows spectra of two samples of hydrothermally altered rocks collected in mining districts of Nevada. The main feature of each spectrum is the intense silicon-oxygen stretching band located between 8 and 9.6 microns. As would be expected for these samples the ν_2 mode for water is seen near 6.2 microns in each trace. A weak peak corresponding to carbonate appears near 6.9 microns in the lower trace of Fig. 7.

Spectra of Surficial Agents

In the locale (East Pioneer Mountains, Montana) where the sample of Fig. 8 was collected, approximately 38 species of lichen were identified and certain areas were estimated to have up to 80% lichen cover. A comparison of the upper and lower curves of Fig. 8 illustrates the extent to which lichen growth can alter the spectral characteristics of a rock sample. The lower trace corresponds to a bare region on the sample whereas the curves in the upper half of the figure were recorded on two areas covered with different species of lichen growth. Although one species was red and the other black, their infrared specta are almost superimposeable. However, examination of the upper spectral traces would provide few clues that the sample was predominantly rock material with but a thin encrustation of biomass. Remotely sensed thermal data in such regions could be expected to be especially difficult to interpret.

Desert varnish is a dark coating of clay and ferromanganese oxides that forms on exposed rock surfaces in arid regions. Desert varnish forms by the accretion of aeolian materials and its composition is independent of that of the underlying rock. Elvidge and Collet[7] found that visible spectra of desert varnish vary little from rock type to rock type and thus tend to obscure rock lithologies in remote sensing. These authors found that varnished rocks all appeared similar to fresh basalt. However the PBDS spectra shown in Fig. 9 indicate that desert varnish does not greatly affect rock spectral characteristics in the middle infrared. Although there is some increased absorption in the silicate band near 9.5 microns, the effect is not great, and the overall shape of the spectrum is very similar to that of the fresh rock substrate. This result suggests that varnishing would not significantly affect remote sensing data in the middle infrared.

5. SUMMARY AND CONCLUSIONS

The foregoing results suggest that PBDS has considerable potential for infrared spectral characterization of geologic materials, particularly in situations where the spectral properties of the outermost surface layers of a material are of interest, e.g. remote sensing applications, studies of weathering, varnishing etc. For such studies conventional absorption/transmission techniques do not provide the required information since no distinction between bulk and surficial spectral properties can be made. Reflectance measurements can provide some surficial information but are complicated by strong absorption and high dependence on the physical state of the sample, e.g. particle size. Specular reflectance measurements in the infrared generally require sample surface polishing, however many naturally occurring materials do not polish well, e.g. rocks having a high clay content. Diffuse reflectance measurements can be applied to very finely powdered samples, but diffuse reflectance spectroscopy of coarse powders, granules or macro samples provides highly variable and difficult to interpret spectra.

Since many natural materials of interest in remote sensing absorb strongly in the middle infrared, an absorbance measuring technique such as PBDS appears to a logical approach to the spectral study of such samples. However the technique is not completely trouble free and certain precautions must be observed. Morterra, et. al.[8] have shown that photothermal spectra can be seriously distorted with samples for which specular reflection is significant. Such samples include single large crystals as well as large grained polymineralic samples such as granitic materials. With these samples decreased absorption in regions of high specular reflectance serves to diminish the photothermal effect often resulting in 'negative' PBDS bands superimposed on positive bands. Thus spectral peaks can be split in two. On the other hand diffuse reflection, which becomes more important as the

effective particle size becomes smaller, results in increased photothermal signal strength, an effect probably due to increased efficiency of heat transfer from sample to the surrounding medium.

Thus although PBDS appears prone to some of the afflictions of diffuse reflection spectroscopy, these problems seem more than outweighed by the ability to examine materials that cannot be studied by conventional means.

6. REFERENCES

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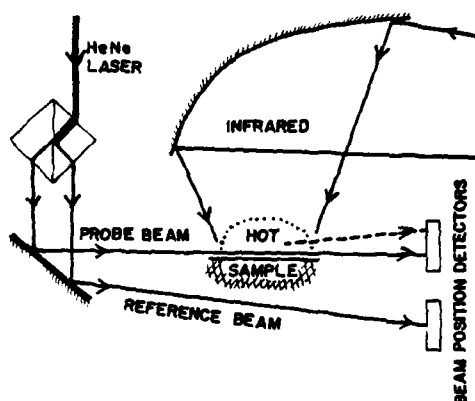
7. FIGURES

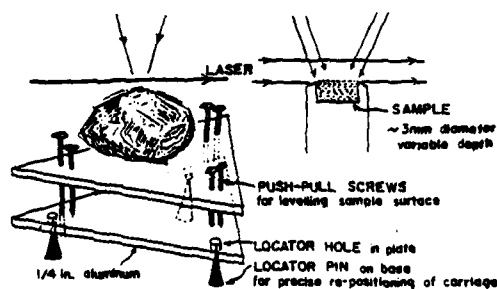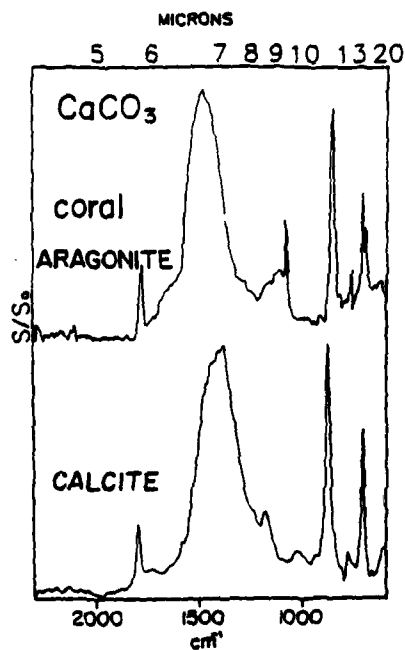Fig. 1 Compensated mirage detector.

Fig. 2 Sample holder.

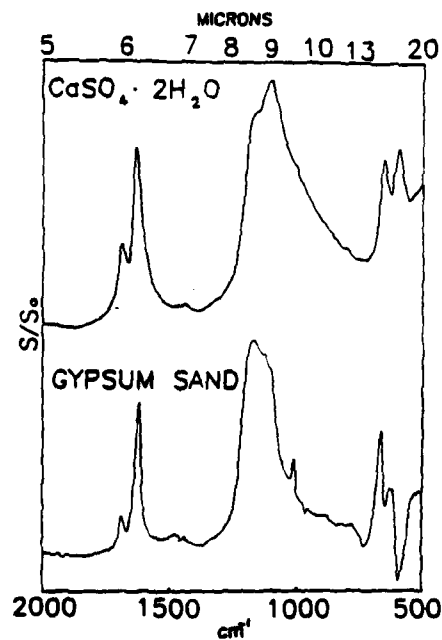Fig. 3 Infrared spectra of two
modifications of calcium carbonate.
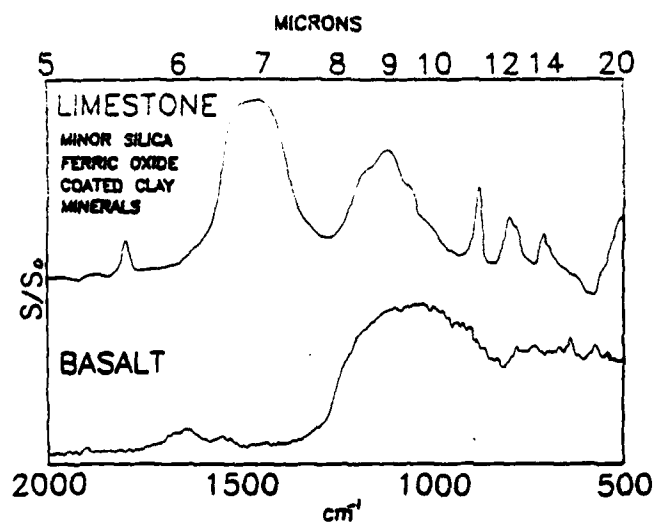

Fig. 4 Infrared spectra of
hydrous calcium sulfate.

MICRONS

5   6   7   8 9 10 12 14 20

LIMESTONE

MINOR SILICA
FERRIC OXIDE
COATED CLAY
MINERALS

S/S_o

BASALT

2000   1500   1000   500

cm^{-1}

Fig. 5 Infrared spectra of
sedimentary and igneous rocks.

MICRONS

5   6   7 8 9 10 12 15 20

KIMBERLITE

OLIVINE
PYROXENE
SERPENTINE
CARBONATE
GARNET
ILMENITE

S/S_o

ALUNITE

2000   1500   1000   500

cm^{-1}
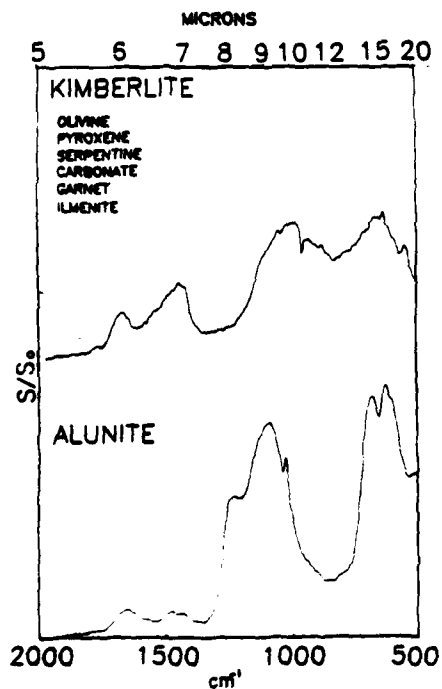
Fig. 6 Infrared spectra of
kimberlite and alunite.

MICRONS

5   6   7 8 9 10   15 20

HYDROTHERMALLY ALTERED

QUARTZ – SOME OPALIZED
FELDSPAR
CLAY MINERALS – MAJOR

S/S_o

CRISTABOLITE – MAJOR
QUARTZ – TRACE
ALUNITE
CALCITE

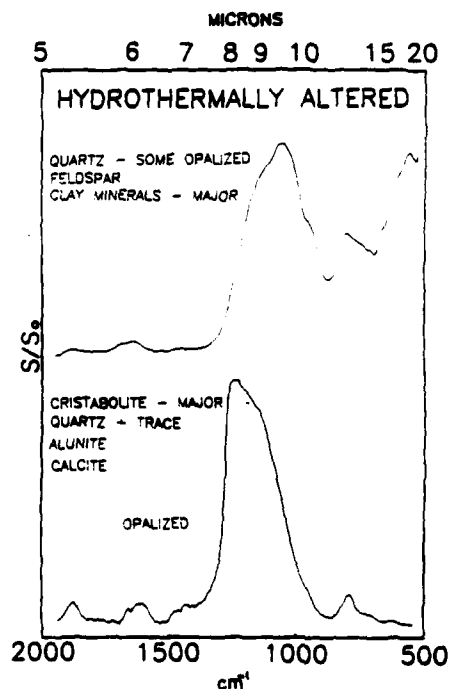OPALIZED

2000   1500   1000   500

cm^{-1}

Fig. 7 Infrared spectra of
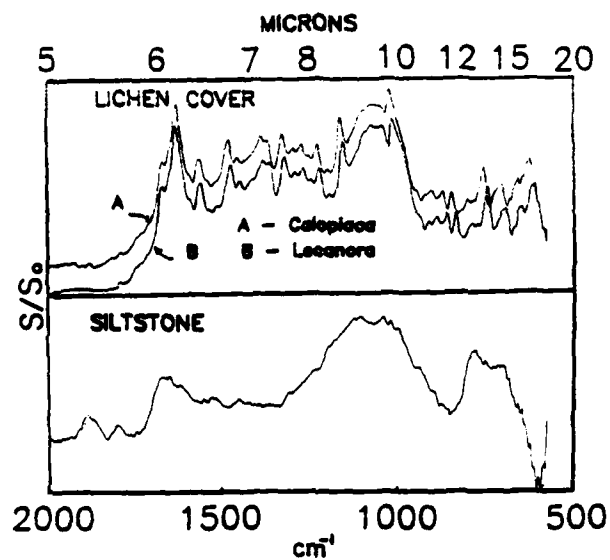hydrothermally altered rocks.

Fig. 8 Infrared spectra of
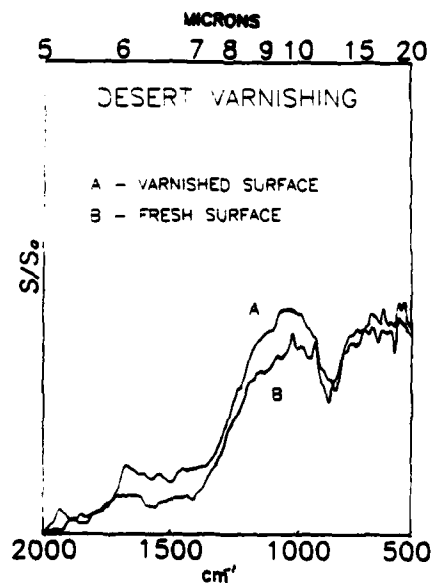lichen growth and substrate
rock.

Fig. 9 Infrared spectra of
varnished and fresh surfaces
of igneous rock.